Vapor-Liquid Equilibrium Data for Binary System Diethylene Glycol Divinyl Ether–Diethylene Glycol Diethyl Ether at Reduced Pressure of 10 Mm. of Mercury

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THE BINARY systems which permit an easy and exact determination of the rectification efficiency of low pressure columns are rare compared with the systems which are used for the same study at atmospheric pressure. Besides, they are generally not easily available or are hard to prepare, such as the systems dodecane-cyclohexylcyclopentane and tridecane-dicyclohexyl (2). Other authors have suggested the systems *n*-decane-*trans*-Decalin and *n*-hexadecane-heptyl benzoate (7).

A test mixture suitable for measuring rectification efficiency of low pressure columns should meet the following requirements.

The relative volatility, α, of this mixture must be suited to the number of plates of the column. For a column having a moderately high efficiency, about 10 plates, a system of rather high relative volatility may be used. Inversely, if the provided number of plates is high, it is necessary to use a system of very small relative volatility.

The mixture of the two components should be accurately analyzable, preferably by a rapid and simple physical method which requires only a small sample.

The components should be readily available and easy to purify.

Finally, if a study at reduced pressure is to be made, it is better to use components, the boiling points of which are neither too high nor too low.

The system ethylbenzene-chlorobenzene is suitable at reduced pressures of about 100 mm. of mercury. At 10 mm. the boiling points of the two components are too low (930° C.) and it is necessary to condense with special cooling.

The binary system diethylene glycol divinyl ether-diethylene glycol diethyl ether agrees with these different requirements. The relative volatility is not too high (α = 1.4) and it is possible to determine the rectification efficiency at reduced pressure of a column having about 15 plates. Besides, such a mixture may be analyzed with accuracy by measuring the refractive index. The index of the divinyl ether is 1.4472 and of the diethyl ether is 1.4128; this difference permits accurate analysis wihtout any error: A difference of 0.0002 on n^{20}_{D} corresponds to a Δx of 0.006. Finally, the boiling points of the two components vary between 60° and 80° C. in the range 1 to 10 mm. of mercury; they are also moderately high and the head vapors may be condensed easily without special cooling.

PURITY OF COMPONENTS

Diethylene glycol divinyl ether is obtained by vinylation of diethylene glycol, and is purified by careful rectification.

Diethyl ether is obtained by hydrogenation of the preceding component and purified by careful rectification.

The physical constants of these products are indicated in Table I, with some literature data.

VAPOR PRESSURE

The vapor pressures of components not found in the literature have been determined in the laboratory. The apparatus is based on the principle of the isoteniscope (4).

A small amount of product is introduced into a vessel which is connected with a U-tube and the equipment is connected with a manometer by the interposition of a cooler. The sample is first boiled under a slight vacuum until no more air bubbles through the U-tube liquid. Then the equipment is connected with the pressure-control system. The U-tube and the vessel are dipped into a bath which is gradually heated. Some air is let into the apparatus until the liquid levels in the U-tube are alike and the temperature and pressure on the manometer are read. However, for the very low pressures, from 5 to 20 mm. of mercury, mercury has been replaced by a liquid of rather low volatility and low density, dibutyl phthalate, which considerably increases the precision of measurements.

Table I. Physical Constants of Compounds

	Diethyl Ether		Divinyl Ether	
	Exptl.	Lit. (3)	Exptl.	Lit. (1)
Density, $^{20}_{4}$	0.9076	0.907	0.9753	...
Refractive index, n^{20}_{D}	1.4128	...	1.4472	...
Boiling point at 760 mm. Hg , ° C.	187.8	188	196.5	196-98

The results are given in Table II and Figure 1. They are represented by the following relations:

$$\text{Diethyl ether } \log p = 8.345 - 2525/T \text{ (mm. Hg)}$$

$$\text{Divinyl ether } \log p = 8.450 - 2610/T \text{ (mm. Hg)}$$

The precision is about 1%.

For interpolation the lines have been plotted on a large scale diagram.

ANALYSIS OF SAMPLES

The samples were analyzed by measuring the refractive index; the curve n^{20}_{D} *vs.* x was determined previously (Table III and Figure 2).

Table II. Vapor Pressures of Components

	Diethylene Glycol Diethyl Ether								
P, mm. Hg	5	10	20	40	60	100	200	400	760
T, ° C.	57.1	70.7	86.1	101.5	112.1	125.1	144.7	166.4	187.8
	Diethylene Glycol Divinyl Ether								
P, mm. Hg	5	10	20	40	60	100	200	400	760
T, ° C.	63.7	77.7	92	108.2	118.7	131.9	152.2	174	196.5

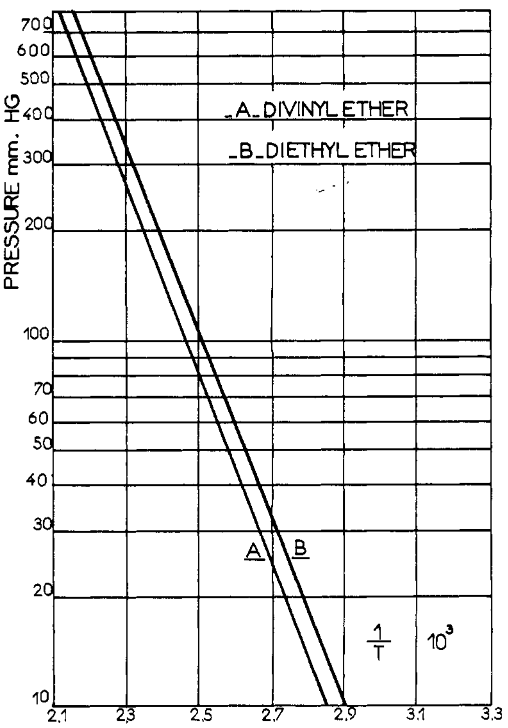

Figure 1. Vapor pressure of pure components

Table III. Refractive Index *vs.* Molecular Composition

Molecular Composition Diethyl Ether	Refractive Index, n^{20}_{D}
0	1.4472
0.100	1.4437
0.200	1.4403
0.400	1.4334
0.500	1.4300
0.600	1.4266
0.800	1.4198
0.900	1.4164
1	1.4128

LIQUID-VAPOR EQUILIBRIUM

Experimental Procedure. The liquid-vapor equilibrium data were determined using Stage's apparatus (*5*) connected with a control manometer and vacuum equipment (Figure 3).

The accuracy of Stage's apparatus has sometimes been denied, because a slight fractionating power was attributed to it; however, the results obtained with this apparatus in the laboratory for different, well known systems agree with literature data.

The liquid sample is introduced into a flask, the upper part of which is connected with an upright cooler. The condensed vapors are collected in an annular receiver which surrounds the collar of the flask. Vacuum is made by means of the pump, P_1. The control system consists of two U-manometers, the former with mercury, the latter with dibutyl phthalate. Two surge tanks are provided, the former between Stage's apparatus, *A*, and the phthalate manometer, *C*, and the latter between *C* and a second vacuum pump, P_2 (tank *D*). The pressure into tank *D* is read by means of the mercury manometer and maintained constant by a vacuum regulator.

When the liquid has been introduced into the flask, the apparatus is evacuated by pump P_1. At the same time, with pump P_2 and the regulator, a pressure of 20 mm. of mercury is maintained in tank *D*. Then one needs only to regulate pressure in apparatus *A* and in tank *B* so as to read on manometer *C* a difference of level of 130 mm. which corresponds to 100 mm. of mercury. Thus the errors which come from the inaccuracy of the reading are greatly decreased and an error of ±2.5 mm. corresponds to a precision of ±0.2 mm. of mercury.

The liquid is heated to boiling for about 2 hours. After this time, a liquid phase sample is drawn out of *E* and a sample of the condensed vapor phase out of *F*. These samples are analyzed by measurement of the refractive index.

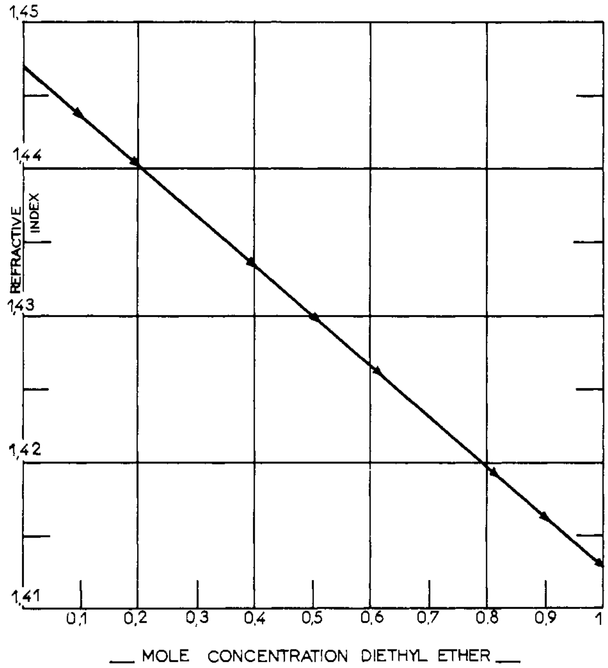

Figure 2. Refractive index *vs.* mole concentration

The temperature is determined with an iron-constantan thermocouple, with a precision to ±0.1° C.

RESULTS

The experimental results are presented in Table IV and Figures 4 and 5.

The binary system diethylene glycol divinyl ether–diethylene glycol diethyl ether may be considered an ideal system. Its average relative volatility is 1.380.

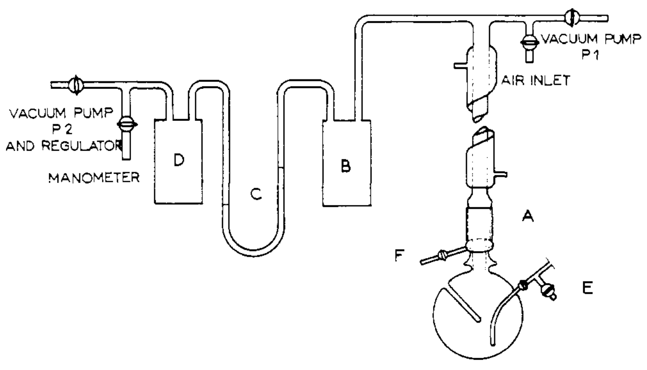

Figure 3. Vapor-liquid equilibrium apparatus

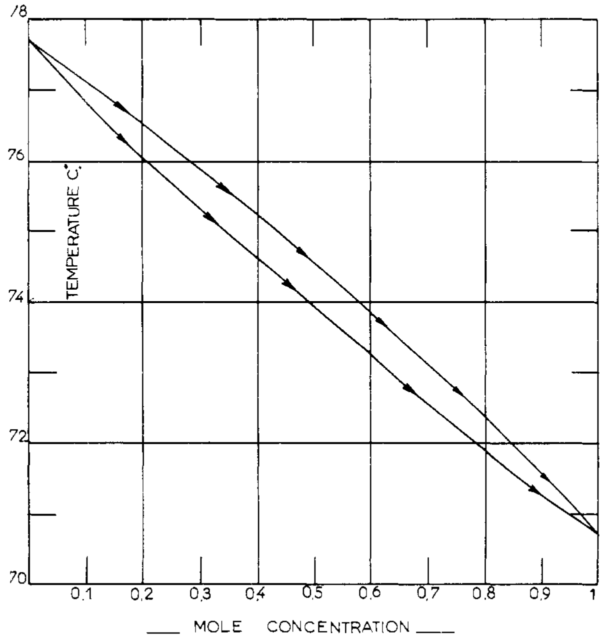

Figure 4. Temperature vs. composition

Binary system diethylene glycol divinyl ether–diethylene glycol diethyl ether

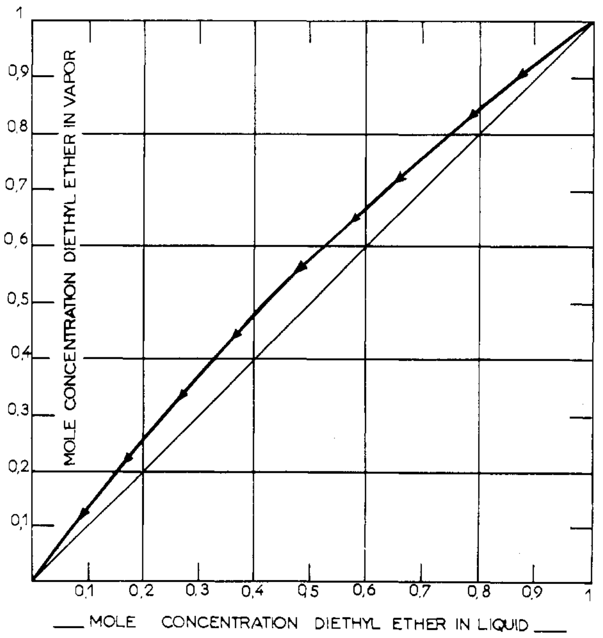

Figure 5. Vapor-liquid relationships at 10 mm. of mercury

Binary system diethylene glycol divinyl ether–diethylene glycol diethyl ether

Table IV. Liquid-Vapor Equilibrium Data at 10 Mm. of Mercury for Binary System Divinyl-Diethyl Ether

T, ° C.	x_1	y_1	p_1^0, Mm. Hg	p_2^0, Mm. Hg	γ_1	γ_2	α
77.7	0	0	13.81	10	...	...	...
77	0.085	0.120	13.4	9.6	1.023	1.001	1.47
76.4	0.163	0.210	12.89	9.484	1	0.996	1.37
75.6	0.265	0.335	12.51	9.078	1.010	0.998	1.39
75	0.350	0.425	12.03	8.750	1.010	1.010	1.37
74.1	0.482	0.562	11.59	8.395	1.007	1.008	1.38
73.4	0.580	0.650	11.17	8.091	1.003	1.010	1.35
72.9	0.655	0.725	10.97	7.907	1.009	1.008	1.39
71.8	0.828	0.870	10.41	7.448	1.002	1.012	1.39
71.2	0.920	0.941	10.21	7.290	1	1.015	1.39
70.7	1	1	10	7.080	...	...	...

CONCLUSIONS

This system is particularly convenient for the determination of the rectification efficiency of low pressure columns. It deviates very slightly from ideality and its relative volatility is low enough to allow the study of columns having about 15 to 20 theoretical plates.

Compared with the system dibutyl phthalate-dibutyl azelate (*6*) the use of which is also suggested, it has the advantage of a lower boiling range (70° to 80° C. at 10 mm. of mercury instead of 200° to 205° C. for phthalate-azelate). Analysis of the samples is easy, and the difference between the refractive index allows an accurate determination of the composition of the mixtures.

Finally, the preparation of these components from diethylene glycol is easy; this system may be used for testing a laboratory column with a rather high number of theoretical plates.

According to the author's experience, divinyl ether may be polymerized, but only in the presence of a catalyst. No phenomenon of this kind has been observed, even after a long heating time, during this work or during the testing of several rectification columns.

NOMENCLATURE

α = relative volatility = $p_1^0\gamma_1/p_2^0\gamma_2$
p_1^0 = vapor pressure of component 1
p_2^0 = vapor pressure of component 2
γ_1 = activity coefficient of component 1 = $Py_1/p_1^0x_1$
γ_2 = activity coefficient of component 2 = $Py_2/p_2^0x_2$
P = total pressure
x_1 = mole concentration of component 1 in liquid phase
x_2 = mole concentration of component 2 in liquid phase
y_1 = mole concentration of component 1 in vapor phase
y_2 = mole concentration of component 2 in vapor phase
T = boiling point, ° K.

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